

**UNITED STATES PATENT APPLICATION**

**OF**

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**FOR**

**LOW DIELECTRIC CONSTANT THIN FILMS AND CHEMICAL VAPOR DEPOSITION**  
**METHOD OF MAKING SAME**

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### **TECHNICAL FIELD OF THE INVENTION**

The present invention relates to a process for forming low dielectric constant thin films useful as insulating materials in microelectronic device structures. More particularly, the present invention is directed to a CVD process for forming porous, low-dielectric constant, SiOC thin films having dielectric constants of less than 2.7.

### **BACKGROUND OF THE INVENTION**

As the need for integrated circuits for semiconductor devices having higher performance and greater functionality increases, device feature geometries continue to decrease. As device geometries become smaller, the dielectric constant of an insulating material used between conducting paths becomes an increasingly important factor in device performance.

As device dimensions shrink to less than  $0.25\ \mu\text{m}$ , propagation delay, cross-talk noise and power dissipation due to resistance-capacitance (RC) coupling become significant due to increased wiring capacitance, especially interline capacitance between the metal lines on the same level. These factors all depend critically on the dielectric constant of the separating insulator.

The use of low dielectric constant (K) materials advantageously lowers power consumption, reduces cross talk, and shortens signal delay for closely spaced conductors through reduction of both nodal and interconnect line capacitances. Dielectric materials, which exhibit low dielectric constants, are critical in the development path toward faster and more power efficient microelectronics.

Silicon oxide ( $\text{SiO}_2$ ), with a dielectric constant of approximately 4, has long been used in integrated circuits as the primary insulating material. However, the interconnect delay associated with  $\text{SiO}_2$  is a limiting factor in advanced integrated circuits.

In order to produce faster and more power efficient microelectronics with smaller device geometries, insulating materials having dielectric constants of less than 3.0 are necessary.

One approach to lowering the dielectric constant of the  $\text{SiO}_2$  insulating layer is by incorporation of carbon. Carbon incorporation from between 15-20%, reduces the dielectric constant to as low as 2.7, in part due to the substitution of the highly polarized Si-O link by Si-C, (i.e., Nakano, et

al., "Effects of Si-C Bond Content on Film Properties of Organic Spin-on Glass" J. Electrochem. Soc., Vol. 142, No. 4, April 1995, pp. 1303-1307).

Alkyl silanes, alkoxy silanes and cyclic-siloxanes such as 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS) are being evaluated aggressively for obtaining low dielectric constant (k) thin-films as interlayer dielectrics in an integrated circuit by a PECVD approach. The resulting films formed when using these precursors give dense SiOC containing films, having dielectric constants in the range of from about 2.7 to 3.0.

A second approach to lowering the dielectric constant is to use porous, low-density, silicon oxide materials in which a fraction of the bulk volume of the SiO<sub>2</sub> film contains air, which has a dielectric constant of 1.

As an example, silica aerogels are porous solids having dielectric constants in the range of from about 2.0 to 1.01 (i.e., Lu, et al., "Low dielectric Constant Materials-Synthesis and Applications in Microelectronics", Mat. Res. Soc. Sym. Proc., April 17-19, San Francisco, CA, 1995, pp. 267-272). The silica aerogels are prepared by sol-gel techniques, which are not well adapted for high-throughput semiconductor processing environments, due to long processing times, saturated alcohol atmospheres, and, in many applications, high pressures for supercritical solvent extraction.

Chemical vapor deposition (CVD) is the thin film deposition method of choice for large-scale fabrication of microelectronic device structures, and the semiconductor manufacturing industry has extensive expertise in its use.

It would therefore be a significant advance in the art to provide a high throughput CVD process, for producing low dielectric constant, silica thin films on a substrate, having dielectric constants less than 3.0.

It therefore is an object of the present invention to provide such process for producing low dielectric constant silica thin films on a substrate, having dielectric constants less than 3.0.

Other objects and advantages of the present invention will be more fully apparent from the ensuing disclosure and appended claims.

### SUMMARY OF THE INVENTION

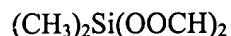
The present invention is directed to the formation of a porous, low dielectric constant SiOC thin film by a process which comprises chemical vapor depositing on a substrate an organosilicon thin film, containing cleavable organic functional groups that upon activation rearrange and cleave as highly volatile liquid and/or gaseous species, to produce a porous, SiOC, thin film having a dielectric constant of less than 3.0.

As used herein, the term "low dielectric constant" refers to a dielectric material with a value of the dielectric constant,  $k$ , below 3.0 as measured at a frequency of 1 mega-Hertz. The term "thin film" refers to a film having a thickness in the range of from about 1000 Å to about 2 μm and the term "SiOC" refers to a thin film composition comprising from about 1 to about 40 atomic percent silicon, preferably from about 20 to 40 percent silicon, from about 1 to about 60 atomic percent oxygen, preferably from about 40 to 60 percent oxygen and from about 1 to about 20 atomic percent carbon and preferably from 5 to 17 percent carbon.

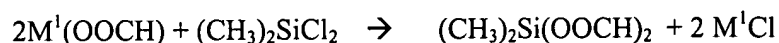
In one aspect, the present invention relates to an organosilicon precursor useful for producing porous, low-dielectric constant, SiOC thin films, wherein the organosilicon precursor comprises at least one cleavable, organic functional group that upon activation rearranges, decomposes and cleaves as a highly volatile liquid or gaseous by-product.

As used herein, the term cleavable refers to an organic functional group, bonded to the silicon atom of the organosilicon precursor that when activated (i.e., thermal, light or plasma enhanced), rearranges, decomposes and/or is liberated as a volatile liquid or gaseous by-product, i.e. CO<sub>2</sub>.

In a preferred aspect of the invention the organosilicon precursor is di(formato)dimethylsilane, a novel composition useful for the deposition of low dielectric constant thin films, comprising the formula:



In a further aspect, the present invention relates to a method of synthesizing di(formato)dimethylsilane by a method comprising:



wherein M<sup>1</sup> is selected from the group consisting of Na (sodium), K (potassium) and Ag (silver).

In a further aspect the present invention relates to a CVD process for producing a porous, low dielectric constant, SiOC thin film on a substrate, from at least one organosilicon precursor comprising at least one cleavable, organic functional group that upon activation, rearranges, decomposes and cleaves as a highly volatile liquid or gaseous by-product.

In yet another aspect, the present invention relates to a porous, dielectric, SiOC thin film produced by the process as described hereinabove.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows a simplified schematic representation of a process system for forming a low k dielectric film on a substrate in accordance with one embodiment of the invention.

Figure 2 shows a simplified schematic representation of a process system for forming a low k dielectric thin film on a substrate in accordance with a further embodiment of the invention.

Figure 3 shows a mass spectroscopic analysis of di(formato)dimethylsilane.

### **DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF**

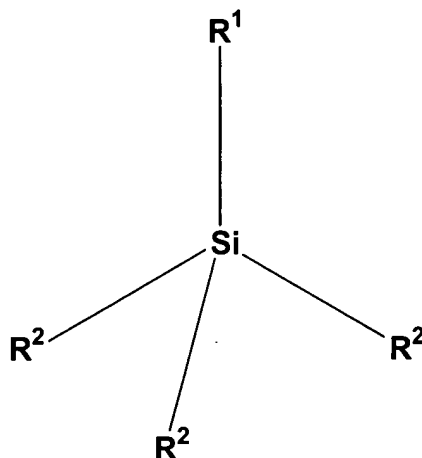
The present invention contemplates the use of organosilicon precursors for CVD formation of porous low dielectric constant thin films, in which the composition contains at least one cleavable organic group that upon activation, rearranges, decomposes and/or cleaves as a highly volatile liquid or gaseous by product.

The organosilicon precursor compositions useful in the invention include compounds having at least one substituent that upon activation, rearranges, decomposes rearranges and/or cleaves as a highly volatile liquid or gaseous by-product.

In one embodiment (hereafter referred to as Embodiment 1) the invention relates to organosilicon precursors for producing porous, low dielectric constant, SiOC thin films, wherein the composition of the organosilicon precursor comprises at least one cleavable organic group that

upon activation, rearranges, decomposes and/or cleaves as a highly volatile liquid or gaseous by product.

In a further embodiment (hereafter referred to as Embodiment 2) the invention relates to organosilicon precursors useful for producing porous, low dielectric constant, SiOC thin films, comprising the general formula:

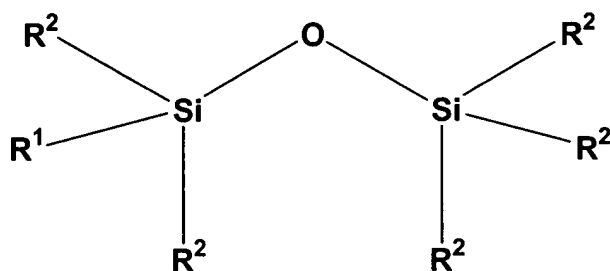


**Formula 1**

wherein

R¹ is a cleavable organic functional group, selected from the group consisting of C₂ to C₆ alkene, C₂ to C₆ alkyne, C₃ to C₄ allyl, C₁ to C₆ alkyl, C₁ to C₆ perfluoroalkyl; ligand X as described hereinbelow, and ligand Y as described hereinbelow; and

each of R² is same or different and each of R² is selected from the group consisting of H, ligand X as described hereinbelow, ligand Y as described hereinbelow, C₂ to C₆ alkene, C₂ to C₆ alkyne, C₃ to C₄ allyl, C₁ to C₆ alkyl, C₁ to C₆ perfluoroalkyl, C₁ to C₆ alkoxy, aryl, perfluoroaryl and C₂ to C₆ alkylsilane; and



**Formula 2**

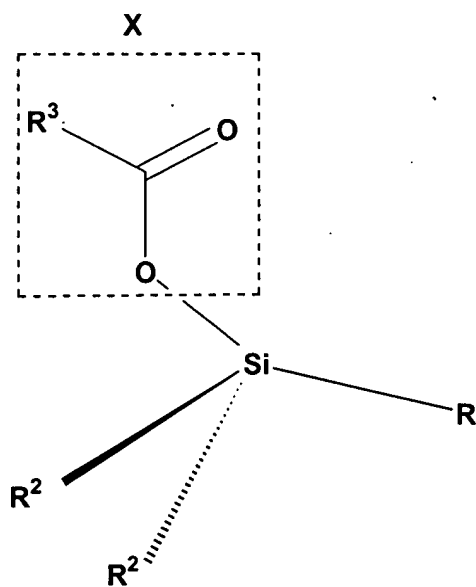
wherein

$\text{R}^1$  is a cleavable organic functional group, selected from the group consisting of  $\text{C}_2$  to  $\text{C}_6$  alkene,  $\text{C}_2$  to  $\text{C}_6$  alkyne,  $\text{C}_3$  to  $\text{C}_4$  allyl,  $\text{C}_1$  to  $\text{C}_6$  alkyl,  $\text{C}_1$  to  $\text{C}_6$  perfluoroalkyl; ligand X as described hereinbelow, and ligand Y as described hereinbelow; and

each of  $\text{R}^2$  is same or different and each of  $\text{R}^2$  is selected from the group consisting of H, ligand X as described hereinbelow, ligand Y as described hereinbelow,  $\text{C}_2$  to  $\text{C}_6$  alkene,  $\text{C}_2$  to  $\text{C}_6$  alkyne,  $\text{C}_3$  to  $\text{C}_4$  allyl,  $\text{C}_1$  to  $\text{C}_6$  alkyl,  $\text{C}_1$  to  $\text{C}_6$  perfluoroalkyl,  $\text{C}_1$  to  $\text{C}_6$  alkoxy, aryl, perfluoroaryl and  $\text{C}_2$  to  $\text{C}_6$  alkylsilane.

In a further embodiment (hereafter referred to as Embodiment 3) the invention relates to organosilicon precursors useful for producing porous, low dielectric constant, SiOC thin films, wherein the organosilicon precursor comprises a composition containing at least one alkyl group and at least one organic functional group that upon activation, rearranges, decomposes and/or cleaves as a highly volatile liquid or gaseous by product.

In a further embodiment (hereafter referred to as Embodiment 4) the invention relates to organosilicon precursors for producing porous, low dielectric constant, SiOC thin films, comprising the general formula:

**Formula 3**

wherein

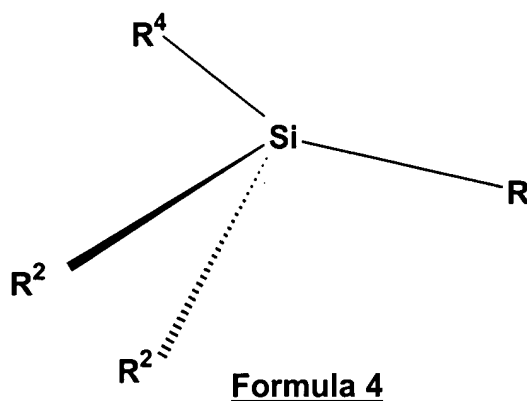
ligand X is a cleavable organic functional group as depicted in Formula 3;

R<sup>3</sup> is selected from the group consisting of: H, C<sub>1</sub> to C<sub>6</sub> alkyl, C<sub>1</sub> to C<sub>6</sub> perfluoroalkyl, C<sub>1</sub> to C<sub>6</sub> carboxylate, aryl and perfluoroaryl;

R is selected from the group consisting of: C<sub>1</sub> to C<sub>4</sub> alkyl and C<sub>1</sub> to C<sub>4</sub> perfluoroalkyl; and

each of R<sup>2</sup> is same or different and each of R<sup>2</sup> is selected from the group consisting of H, ligand X as described hereinabove, ligand Y as described hereinbelow, C<sub>2</sub> to C<sub>6</sub> alkene, C<sub>2</sub> to C<sub>6</sub> alkyne, C<sub>3</sub> to C<sub>4</sub> allyl, C<sub>1</sub> to C<sub>4</sub> alkyl, C<sub>1</sub> to C<sub>4</sub> perfluoroalkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, aryl, perfluoroaryl and C<sub>2</sub> to C<sub>6</sub> alkylsilane;



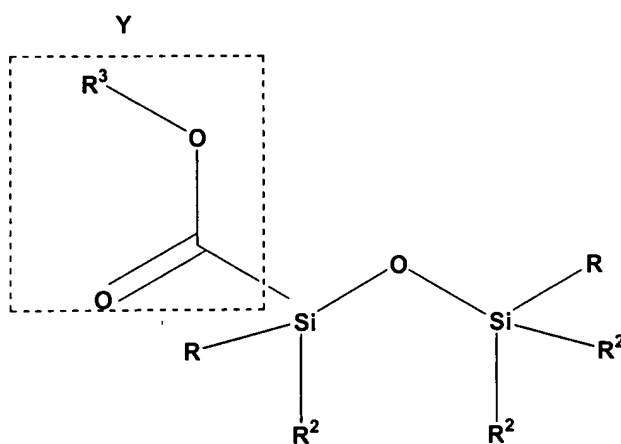


wherein

$R^4$  is a cleavable organic functional group selected from the group consisting of:  $C_2$  to  $C_6$  alkene, and  $C_2$  to  $C_6$  alkyne,  $C_3$  to  $C_4$  allyl,  $C_1$  to  $C_6$  alkyl,  $C_1$  to  $C_6$  perfluoroalkyl;  $C_1$  to  $C_6$  alkylsilane, and ligand Y as described hereinbelow;

R is selected from the group consisting of:  $C_1$  to  $C_4$  alkyl and  $C_1$  to  $C_4$  perfluoroalkyl; and

each of  $R^2$  is same or different and each of  $R^2$  is selected from the group consisting of H, ligand X as described hereinabove, ligand Y as described hereinbelow,  $C_2$  to  $C_6$  alkene,  $C_2$  to  $C_6$  alkyne,  $C_3$  to  $C_4$  allyl,  $C_1$  to  $C_4$  alkyl,  $C_1$  to  $C_4$  perfluoroalkyl,  $C_1$  to  $C_6$  alkoxy, aryl, perfluoroaryl and  $C_2$  to  $C_6$  alkylsilane;



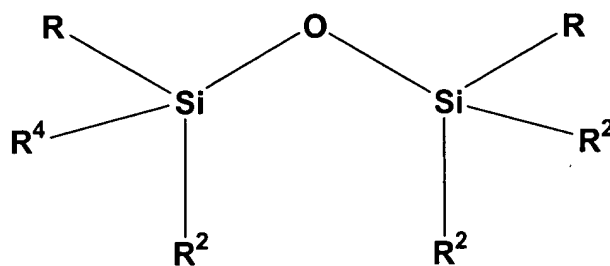
wherein

ligand Y is a cleavable organic functional group as depicted in Formula 3;

$R^3$  is selected from the group consisting of: H,  $C_1$  to  $C_6$  alkyl,  $C_1$  to  $C_6$  perfluoroalkyl aryl; perfluoroaryl and  $C_1$  to  $C_6$  carboxylate;

R is selected from the group consisting of:  $C_1$  to  $C_4$  alkyl and  $C_1$  to  $C_4$  perfluoroalkyl; and

each of  $R^2$  is same or different and each of  $R^2$  is selected from the group consisting of H, ligand X as described hereinabove, ligand Y as described hereinbelow,  $C_2$  to  $C_6$  alkene,  $C_2$  to  $C_6$  alkyne,  $C_3$  to  $C_4$  allyl,  $C_1$  to  $C_4$  alkyl,  $C_1$  to  $C_4$  perfluoroalkyl,  $C_1$  to  $C_6$  alkoxy, aryl, perfluoroaryl and  $C_2$  to  $C_6$  alkylsilane;



**Formula 6**

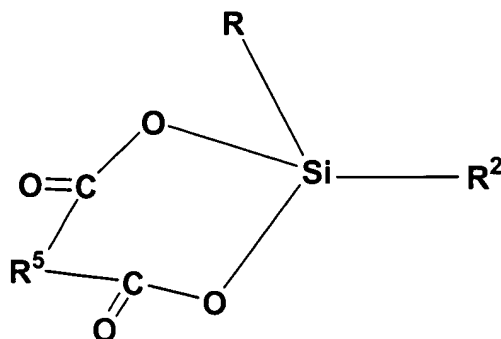
wherein

$R^4$  is a cleavable organic functional group selected from the group consisting of:  $C_2$  to  $C_6$  alkene, and  $C_2$  to  $C_6$  alkyne,  $C_3$  to  $C_4$  allyl,  $C_1$  to  $C_6$  alkyl,  $C_1$  to  $C_6$  perfluoroalkyl;  $C_1$  to  $C_6$  alkylsilane, and ligand Y as described hereinabove;

each of R is same or different and each of R is selected from the group consisting of:  $C_1$  to  $C_4$  alkyl and  $C_1$  to  $C_4$  perfluoroalkyl; and

each of  $R^2$  is same or different and each of  $R^2$  is selected from the group consisting of H, ligand X as described hereinabove, ligand Y as described hereinabove,  $C_2$  to  $C_6$  alkene,

C<sub>2</sub> to C<sub>6</sub> alkyne, C<sub>3</sub> to C<sub>4</sub> allyl, C<sub>1</sub> to C<sub>4</sub> alkyl, C<sub>1</sub> to C<sub>4</sub> perfluoroalkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, aryl, perfluoroaryl and C<sub>2</sub> to C<sub>6</sub> alkylsilane; and



**Formula 7**

wherein

R<sup>5</sup> is optional and may be selected from the group consisting of C<sub>1</sub> to C<sub>2</sub> alkyl;

R is selected from the group consisting of: C<sub>1</sub> to C<sub>4</sub> alkyl and C<sub>1</sub> to C<sub>4</sub> perfluoroalkyl; and

R<sup>2</sup> is selected from the group consisting of H, ligand X as described hereinabove, ligand Y as described hereinabove, C<sub>2</sub> to C<sub>6</sub> alkene, C<sub>2</sub> to C<sub>6</sub> alkyne, C<sub>3</sub> to C<sub>4</sub> allyl, C<sub>1</sub> to C<sub>4</sub> alkyl, C<sub>1</sub> to C<sub>4</sub> perfluoroalkyl, C<sub>1</sub> to C<sub>6</sub> alkoxy, aryl, perfluoroaryl and C<sub>2</sub> to C<sub>6</sub> alkylsilane.

Examples of the volatile by-products produced by the activation step of the present invention include but are not limited to:

**Cleavable functional group**

carboxylate

dicarboxylate

alkene

**Volatile by-product**

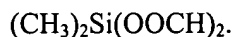
CO, HCOH, CO<sub>2</sub>

CO, HOCH, CO<sub>2</sub>

alkynes, hydrocarbons

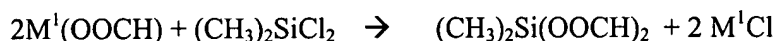
alkyne	hydrocarbons
alkyl	alkene
benzylate	CO <sub>2</sub> , phenyl, benzene

In a preferred embodiment, (hereafter referred to as Embodiment 5) the present invention relates to di(formato)dimethylsilane, a novel organosilicon precursor composition useful for producing low dielectric constant thin films, comprising the formula:



The organosilicon compositions of the invention are usefully employed to form low dielectric constant thin films on substrates by chemical vapor deposition. More particularly diformatodimethylsilane is useful for producing porous, low dielectric constant, SiOC thin films.

In a further embodiment the present invention relates to a method of synthesizing di(formato)dimethylsilane by a method comprising:



wherein M<sup>1</sup> is selected from the group consisting of: Na(sodium), K (potassium) and Ag (silver).

Other synthetic approaches may be usefully employed for the synthesis of di(formato)dimethylsilane with equal success. In no way should the synthetic approach limit the scope of the present invention.

Specific examples of organosilicon precursors useful in the present invention, include but are not limited to:

di(formato)methylsilane; di(formato)dimethylsilane; tri(formato)methylsilane; 1,3, dimethyl 1,1,3,3- tetra(formato)disiloxane; 1,3-di(formato)disiloxane; diethyldimethylsilane; triethylmethylsilane; 1,3-Diethyl-1,3-dimethyldisiloxane; di-t-butylsilane; 1,3-di-t-butyl-1,1,3,3-tetramethyldisiloxane; di-isopropylsilane; 1,3-di-isopropyl-1,1,3,3- tetramethyldisiloxane; di-isobutylsilane; 1,3-di-isobutyl-1,1,3,3,- tetramethyldisiloxane; t-butylsilane; 1,3-di-t-butyl-1,1,3,3- tetramethyldisiloxane; 1, 3-diethyny-1,1,3,3-tetramethyldisiloxane; 1, 3-diethynyldimethyldisiloxane; 1,3-divinyl-1,1,3,3-tetramethyldisiloxane and 1,3-divinyl-1,3-dimethyldisiloxane.

Most organosilicon precursors of the present invention are available commercially through Gelest, Inc., a leading supplier of silanes, or such precursors may be readily synthesized using methods that are well known in the art.

In a further embodiment, (hereafter referred to as Embodiment 6) the present invention relates to a chemical vapor deposition (CVD) process and more preferably a plasma enhanced chemical vapor deposition (PECVD) process for forming a low dielectric constant thin film on a substrate, including the steps of:

placing the substrate in a chemical vapor deposition apparatus,

introducing at least one vaporized organosilicon precursor comprising at least one cleavable organic functional group into the apparatus;

transporting the organosilicon vapor into a chemical vapor deposition zone containing a substrate, optionally using a carrier gas to effect such transport;

contacting the organosilicon vapor with the substrate under chemical vapor deposition conditions to deposit a thin film comprising an organosilicon composition; and

annealing the organosilicon thin film to produce a porous, SiOC, low dielectric constant thin film.

In a preferred embodiment the organosilicon thin film of Embodiment 6 retains between 1 and 100 percent of the cleavable, organic functional groups, more preferably the organosilicon thin film retains between about 25 to 100 percent of the cleavable organic functional groups and most preferably, the organosilicon thin film retains between about 50 to 100 percent of the cleavable organic functional groups.

In yet a further embodiment, (hereafter referred to as Embodiment 7) the present invention relates to a CVD process and more preferably a PECVD process, for forming low dielectric constant thin films on a substrate, including the steps of:

placing the substrate in a chemical vapor deposition apparatus;

introducing at least one vaporized organosilicon precursor comprising at least one cleavable organic functional group and at least one alkyl group into the apparatus;

transporting the organosilicon vapor into a chemical vapor deposition zone containing a substrate, optionally using a carrier gas to effect such transport;

contacting the organosilicon vapor with the substrate under chemical vapor deposition conditions to deposit a thin film comprising an organosilicon composition;

annealing the organosilicon thin film to produce a porous, SiOC, low dielectric constant thin film.

In a preferred embodiment the organosilicon thin film of Embodiment 7 retains between 1 to 100 percent of the cleavable, organic functional groups and between 1 to 100 percent of the alkyl groups; more preferably the organosilicon thin film retains between about 25 to 100 percent of the cleavable organic functional groups and between about 25 to 100 percent of the alkyl groups; and most preferably, the organosilicon thin film retains between about 50 to 100 percent of the cleavable organic functional groups and between about 50 to 100 percent of the alkyl groups.

The annealing step of Embodiments 6 and 7 is carried out at a temperature in the range of from about 100°C to about 400°C, optionally in the presence of an oxidizing or reducing gas, for a length of time and under conditions sufficient to effect the removal of the cleavable, organic functional groups and optionally a portion of the alkyl groups (if present) to produce a porous, SiOC thin film having a dielectric constant of less than 3.0.

The annealing step of Embodiments 6 and 7 may further comprise plasma enhanced conditions, at a temperature in the range of from about 100 to about 400°C, optionally in the presence of an oxidizing or reducing gas, for a length of time and under conditions sufficient to effect the removal of the volatile organic groups and optionally a portion of the alkyl groups, to produce a porous, SiOC thin film having a dielectric constant of less than 3.0.

In a further embodiment (hereafter referred to as "Embodiment 8") the present invention relates to an organosilicon precursor vapor comprising from about 1 to about 100% by volume of an

organosilicon composition as described in Embodiments 1-4, and from about 0 to about 99% by volume of an inert carrier gas, based on the total volume of organosilicon precursor vapor and the inert carrier gas, is subjected to chemical vapor deposition (CVD) conditions, preferably plasma enhanced chemical vapor deposition conditions, in a chamber containing a substrate, so that the precursor composition in vapor or plasma form is contacted with the substrate in the CVD chamber to deposit thereon, a dense SiOC thin film comprising cleavable organic functional groups.

In a further embodiment (hereafter referred to as "Embodiment 9") the present invention relates to an organosilicon precursor vapor comprising from about 1 to about 100% by volume of an organosilicon composition as described in Embodiments 3-4, and from about 0 to about 99% by volume of an inert carrier gas, based on the total volume of organosilicon precursor vapor and the inert carrier gas, is subjected to chemical vapor deposition (CVD) conditions, preferably plasma enhanced chemical vapor deposition conditions, in a chamber containing a substrate, so that the precursor composition in vapor or plasma form is contacted with the substrate in the CVD chamber to deposit thereon, a dense SiOC thin film comprising alkyl groups and cleavable organic functional groups.

In a further embodiment (hereafter referred to as "Embodiment 10") an organosilicon precursor vapor comprising from about 1 to about 100% by volume of an organosilicon composition as described in Embodiments 1-4, from about 0 to about 99% by volume of an inert carrier gas, and from about 1 to about 99% by volume of at least one co-reactant, based on the total volume of organosilicon precursor vapor, inert carrier gas and co-reactant, is subjected to chemical vapor deposition (CVD) conditions, preferably plasma enhanced chemical vapor deposition conditions in a plasma chamber containing a substrate, so that the precursor composition in vapor or plasma form is contacted with the substrate in the CVD chamber to deposit thereon, a dense SiOC thin film comprising cleavable organic functional groups thereon.

In a still further embodiment (hereafter referred to as "Embodiment 11") an organosilicon precursor vapor comprising from about 1 to about 100% by volume of an organosilicon composition as described in Embodiments 3-4, and from about 0 to about 99% by volume of an inert carrier gas and from about 1 to about 99% by volume of at least one co-reactant, based on the total volume of organosilicon precursor vapor, inert carrier gas and co-reactant, is subjected to chemical vapor deposition (CVD) conditions, preferably plasma enhanced chemical vapor

deposition conditions in a plasma chamber containing a substrate, so that the precursor composition in vapor or plasma form is contacted with the substrate in the CVD chamber to deposit thereon, a dense SiOC thin film comprising alkyl groups and cleavable organic functional groups thereon.

For the purpose of depositing the organosilicon thin films of the present invention, the organosilicon compounds may optionally be used in combination with other co-reactants, i.e., other organosilicon precursors of the present invention, other organosilicon precursors, or reactive gases *i.e.* CO<sub>2</sub>, ethylene, acetylene, N<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub> and mixtures thereof.

The inert carrier gas in the processes described hereinabove may be of any suitable type, *i.e.*, argon, helium, etc. or a compressible gas or liquid, *i.e.*, CO<sub>2</sub>.

The processes of Embodiments 6 and 7, may further include subjecting at least one organosilicon precursor as described hereinabove in Embodiments 1-4 to chemical vapor deposition (CVD) conditions in a CVD chamber containing a substrate, so that the precursor composition is deposited in such a form as to retain a portion of the original cleavable organic functional groups, wherein the CVD conditions include temperature in the chamber in a range of from about 50°C to about 400°C and more preferably in a range of from about 250°C to about 350°C, and a chamber pressure in a range of from about 500 mTorr to about 10 Torr, more preferably the chamber pressure is set to about 4 Torr.

Similarly, the processes of Embodiments 7, may further include subjecting at least one organosilicon precursor as described hereinabove in Embodiments 3 and 4 to chemical vapor deposition (CVD) conditions in a CVD chamber containing a substrate, so that the precursor composition is deposited in such a form as to retain a portion of the original alkyl and cleavable organic functional groups, wherein the CVD conditions include temperature in the chamber in a range of from about 50°C to about 400°C and more preferably in a range of from about 250°C to about 350°C, and a chamber pressure in a range of from about 500 mTorr to about 10 Torr, more preferably the chamber pressure is set to about 4 Torr.

In the preferred PECVD process of Embodiments 6-10, the plasma may be generated from single or mixed frequency RF power. The plasma source may comprise a high frequency, radio frequency (HFRF) plasma source component generating power in a range of from about 75 W to



about 200 W at a frequency of about 13.56 MHz or a low frequency radio frequency (LFRF) plasma source component generating power in a range from about 5 W and 75 W at a frequency of about 350 kHz and/or combinations thereof. The plasma is maintained for a period of time sufficient to deposit the dense SiOC thin film having retained therein between 1 to 100 percent of the original alkyl groups and between 1 and 100 percent of the cleavable organic functional groups. In a preferred embodiment, the dense SiOC thin film retains between 50 to 100 percent of the original alkyl groups and between 50 to 100 percent of the original cleavable organic functional groups.

In a preferred embodiment, the deposition process of Embodiments 6-10 is tuned with single frequency or dual frequency operating simultaneously to yield a dense SiOC thin film wherein between 1 and 100 percent of the alkyl groups and between 1 and 100 percent of the cleavable organic functional groups are retained in the deposited film.

In a further embodiment, the dense SiOC film formed in Embodiment 6 or Embodiment 7 is post annealed in a furnace, at a temperature in the range of from about 100°C to about 400°C, optionally in the presence of an oxidizing or reducing gas, for a length of time and under conditions sufficient to effect the removal of at least a portion of the cleavable organic functional groups and a desired portion of the alkyl groups to produce a porous, low dielectric constant, SiOC thin film.

The dense SiOC thin film may be optionally annealed at a gradually increasing temperature profile to effect the rearrangement and volatilization of the cleavable organic groups.

In a preferred embodiment, the dense SiOC thin film is annealed at a temperature of about 400°C.

The post-annealing step as serves to activate the cleavable organic groups retained in the dense SiOC thin film in such a way as to effect the rearrangement and/or decomposition of the cleavable organic groups to form volatile organic liquid or gaseous by-products. A portion of the alkyl groups in the dense SiOC thin film retains the carbon, resulting in Si-C bonds. The final result is a micro-porous, low dielectric constant SiOC thin film.

In a preferred embodiment, the post-annealing step activates the cleavable functional groups by way of a rearrangement process that results in a volatile organic species and forms uniformly distributed pores throughout the thin film.

The carbon concentration of the micro-porous, SiOC thin film may be tailored to give optimum carbon levels that result in a material with a lower dielectric constant and increased hardness, by varying process conditions that are well known to those skilled in the art.

In a further embodiment the post-annealing step occurs under plasma-enhanced or oxygen assisted plasma conditions.

To further promote the rearrangement process, the annealing step may further comprise: co-reactants, such as CO<sub>2</sub>; oxidizing gases, such as O<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O or NO; reducing gases such as H<sub>2</sub> or NH<sub>3</sub>; inert gases, such as He or Ar; and/or combinations thereof.

In one embodiment the micro-porous, low dielectric constant, SiOC thin film of the instant invention comprises between 5 and 99 percent porosity, more preferably between 5 and 80 percent porosity and most preferably between 5 and 70 percent porosity.

The porosity of the micro-porous, SiOC thin film may be tailored to give optimum porosity levels that result in a material with a lower dielectric constant, by varying the percentage of cleavable organic functional groups in the organosilicon precursor(s) and by varying process conditions that are well known to those skilled in the art.

As used herein, the term porosity refers to that fraction of the low dielectric constant thin film that comprises air and includes molecular sized pores in the range of from about 5 to 20 nm, mesopores (between molecules) of less than 150 nm and micropores (within the particle), of less than 2 nm.

In a further embodiment, the micro-porous, low dielectric constant, SiOC thin film comprises between 1 and 20 percent carbon, more preferably between 1 and 15 percent carbon and most preferably between 1 and 10 percent carbon.

In a preferred embodiment the dielectric constant of the porous SiOC thin film produced by any one of the aforementioned embodiments is less than 3.0, more preferably the dielectric constant of the porous SiOC thin film is less than 2.0 and most preferably the dielectric constant of the porous SiOC thin film is less than 1.5.

Specific CVD conditions and more particularly PECVD conditions are readily determinable for a given application by empirically varying the process conditions (e.g., pressure, temperature, flow rate, relative proportions of the organosilicon precursor gas and inert carrier gas in the composition, etc.) and developing correlation to the film properties produced in the process. The conditions of the process as disclosed herein are monitored to retain alkyl and cleavable organic groups in the dense SiOC film.

Figure 1 is a schematic representation of a process system 10 for forming a low k dielectric film on a substrate in accordance with one embodiment of the invention.

In process system 10, a source 12 of organosilicon precursor(s) is joined by line 18 to disperser (*i.e.*, showerhead or aerosol nozzle) 28 in CVD reactor 24. The CVD reactor may be constructed and arranged to carry out CVD involving thermal dissociation of the precursor vapor to deposit the desired SiOC film on the substrate 34 mounted on susceptor 30 heated by heating element 32. Alternatively, the CVD reactor may be constructed and arranged for carrying out plasma-enhanced CVD, by ionization of the precursor gas mixture.

A source 16 of carrier gases is also provided, joined by line 22 to the disperser 28 in CVD reactor 24.

The disperser 28 may comprise a showerhead nozzle, jet or the like which functions to receive and mix the feed streams from the respective sources 12, 14 and 16, to form a gaseous precursor mixture which then is flowed toward the substrate 34 on the heated susceptor 30. The substrate 34 may be a silicon wafer or other substrate element and material, on which the low k dielectric film is deposited.

In lieu of mixing the respective feed streams from lines 18 and 22 in the disperser, the streams may be combined in a mixing vessel or chamber upstream of the CVD reactor 24. Further, it will

be appreciated that if the CVD reactor is configured and operated for carrying out PECVD, a plasma generator unit may be provided as part of or upstream of the CVD reactor 24.

The feed streams from sources 12 and 16 may be monitored in lines 18 and 22, respectively, by means of suitable monitoring devices (not shown in Figure 1), and the flow rates of the respective streams may be independently controlled (by means such as mass flow controllers, pumps, blowers, flow control valves, regulators, restricted flow orifice elements, etc., also not shown) to provide a combined precursor feed stream having a desired compositional character.

The precursor formulations of the invention may be employed in any suitable chemical vapor deposition system to form corresponding thin films on a substrate or microelectronic device precursor structure as a dielectric layer thereon. The CVD system may for example comprise a liquid delivery CVD system, a bubbler-based CVD system, or a CVD system of any other suitable type. Suitable liquid delivery CVD systems include those disclosed in Kirlin et al. U.S. Patent 5,204,134; Kirlin et al. U.S. Patent 5,536,323; and Kirlin et al. U.S. Patent 5,711,816.

In liquid delivery CVD, the source liquid may comprise the source reagent compound(s) or complex(es) *per se*, if the compound(s) or complex(es) are in the liquid phase at ambient temperature (e.g., room temperature, 25°C) or otherwise at the supply temperature from which the source reagent is rapidly heated and vaporized to form precursor vapor for the CVD process. Alternatively, if the source reagent compound or complex is a solid at ambient or the supply temperature, such compound(s) or complex(es) can be dissolved or suspended in a compatible solvent medium to provide a liquid phase composition that can be submitted to rapid heating and vaporization to form precursor vapor for the CVD process. The precursor vapor resulting from the vaporization then is transported, optionally in combination with a carrier gas (e.g., He, Ar, H<sub>2</sub>, O<sub>2</sub>, etc.), to the chemical vapor deposition reactor where the vapor is contacted with a substrate at elevated temperature to deposit material from the vapor phase onto the substrate or semiconductor device precursor structure positioned in the CVD reactor.

In addition to flash vaporizer liquid delivery systems, other reagent delivery systems such as bubblers and heated vessels can be employed. In bubbler-based delivery systems, an inert carrier gas is bubbled through the precursor composition to provide a resulting fluid stream that is wholly or partially saturated with the vapor of the precursor composition, for flow to the CVD tool.

Accordingly, any method that delivers the precursor composition to the CVD tool may be usefully employed.

In a further embodiment, the present invention relates to a porous, dielectric, SiOC thin film produced by the process as described hereinabove in Embodiments 6 and 7. In a preferred embodiment the present invention relates to a porous dielectric thin film produced by the process as described hereinabove in Embodiments 6 and 7, wherein the dielectric constant of the thin film is less than 2. In a more preferred embodiment the present invention relates to a porous dielectric thin film produced by a process as described hereinabove in Embodiments 6 and 7, wherein the dielectric constant of the thin film is less than 1.5.

The following examples are provided to further exemplify the production and usefulness of compounds of the present invention. These examples are presented for illustrative purposes only, and are not in any way intended to limit the scope of the present invention

### **EXAMPLES**

#### **Synthesis of Di(formato)dimethylsilane**

Sodium formate (2mols) is suspended in acetonitrile with continuous stirring at room temperature. Dimethyldichlorsilane (1mol) dissolved in acetonitrile is slowly added to the sodium formate suspension in acetonitrile. The reaction mixture is allowed to stir after addition for an additional hour and refluxed for 30mins. The reaction mixture is filtered and the solvent is removed under reduced pressure by distillation. The crude diformatodimethylsilane is purified by distillation.

#### **PECVD of Di(formato)dimethylsilane**

Figure 2 is a schematic representation of a process system 10 for forming a low k dielectric film on a substrate in accordance with a preferred embodiment of the invention.

Di(formato)dimethylsilane is delivered into a PECVD deposition chamber 38 as a chemical vapor. Optionally, the di(formato)dimethylsilane may be delivered with a carrier gas. The chemical vapor is obtained either by vapor draw or by direct liquid injection of liquid into a vaporizer, which is heated to an elevated temperature.

In a first step, the deposition process is carried out on a substrate 40, typically a silicon wafer, at a temperature in a range of from about 100-400°C in the presence of a single frequency or dual frequency (42) plasma activation. Film properties and deposition parameters are monitored as a function of plasma power, reactor pressure, oxygen to precursor ratio, and deposition temperature. The deposition process is monitored to obtain a film with the desired composition of  $\text{Si}_x\text{O}_y\text{C}_z$ . The process is optimized to retain the highest percentage of the functional groups and a desired percentage of the alkyl groups in the film.

In a second step, the process involves annealing at higher temperatures and or by additional plasma activation. In this step the functional groups are cleaved as volatile gaseous or high vapor pressure liquids that are removed continuously. Preferably, some of the methyl groups are retained in the deposited film. In the case of di(formato)dimethylsilane, the formato group is a cleavable functional group used to generate micro porosity in the resulting thin film. The volatile products generated by rearrangement and/or decomposition of the formato ligand include but are not limited  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_2\text{O}$ .

The cleavable formato ligand contains a  $\beta$ -hydrogen that under conditions as described herein, undergoes a rearrangement process that results in the formation of cleavable volatile products, *i.e.*,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_2\text{O}$ , with high vapor pressure.

Similarly, other molecules containing alkyl and/or other functional groups with  $\beta$ -hydrogens may undergo rearrangements. Such rearrangement process results in formation of cleavable volatile products with high vapor pressures that undergo elimination reactions when subjected to conditions as described herein. Elimination of the organic groups results in microporosity that effectively reduces the dielectric constant of the  $\text{SiOC}$  thin film.

The above-described steps can be carried out either sequentially or separately in order to produce the porous, low dielectric constant thin films of the present invention.

#### **Mass Spectroscopic Analysis of Di(formato)dimethylsilane**

Figure 3 shows a mass spectroscopic analysis of di(formato)dimethylsilane  $(\text{CHOO})_2\text{Si}(\text{CH}_3)_2$ . The mass spectroscopic analysis evidences the fragmentation pattern of the molecule under mass spec conditions. A strong molecular ion peak at  $m/e$  133 reveals loss of one  $\text{CH}_3$  group with

subsequent  $\beta$ -rearrangement of the formate hydrogens and loss of two CO groups as shown by molecular fragments at m/e 105 and m/e 77. The mass specification fragmentation pattern evidences the inherent tendency of the formate groups to rearrange and cleave as volatile by-products.

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Although the invention has been variously disclosed herein with reference to illustrative aspects, embodiments and features, it will be appreciated that the aspects, embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art. The invention therefore is to be broadly construed, consistent with the claims hereafter set forth.